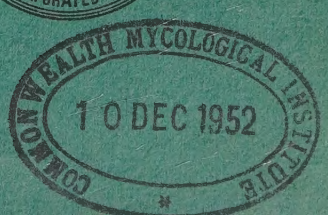
Annual Report for 1951 of the Chemical Division of the Rubber Research Institute of Malaya



FOREWORD

IT HAS BEEN THE CUSTOM to publish annually the reports of the several Divisions of the R.R.I. together with an introductory survey by the Director.

During the period of rehabilitation after the war and subsequently, whilst plans for expansion of the research work of the Institute were being developed, 1949 to 1951, the publication of progress reports has been delayed. Although separate publications on specific subjects of research have been issued from time to time throughout the period, as R.R.I. Journal Communications, formal Annual Reports have not been published.

A general report for the period 1949 to 1951 is now in preparation, this publication will include annual progress reports of the Divisions.

Meantime, in order to avoid further delay in reporting the progress of investigations which have not yet reached the stage for detailed publications, the reports of Divisions for 1951 are to be published separately.

The Report of the Chemical Division for the year 1951 is presented.

Director

CHEMICAL DIVISION 1951

RUBBER RESEARCH INSTITUTE OF MALAYA
KUALA LUMPUR

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STAFF

AT THE COMMENCEMENT of 1951, the graduate staff of the Division comprised Mr M.W. Philpott (Head of the Division), Mr G.W. Drake, Mr A. Walker, Dr R.H. Smith, Mr A.S. Cook, Mr H.M. Edmondson, Mr K.C. Sekar, Mr Cheah Sein Liat, and Mr B.C. Sekhar.

Mr R.S. Gale, Chemical Engineer, took up his duties with the Division early in May.

Seconded staff consisted of the following:

Mr W.G. Wren, *London Advisory Committee for Rubber Research (Ceylon & Malaya).*

Dr G.F. Bloomfield, *The British Rubber Producers' Research Association,* who returned to England early in January.

Dr A.I. McMullen, *The British Rubber Producers' Research Association.*

Mr R.I. Wood, *The British Rubber Producers' Research Association.*

The Head of the Chemical Division, Mr M.W. Philpott, proceeded on long leave in January and resigned his appointment in August. Following Mr Philpott's departure in January, Mr W.G. Wren acted as Head of Division.

Mr G.W. Drake proceeded on long leave in March; it was arranged that he should be seconded for six months to work in the Welwyn laboratories of the British Rubber Producers' Research Association.

INVESTIGATIONS

INTRODUCTION

DURING THE PAST YEAR an attempt has been made to canalise research and development work along a few major lines of investigation, in the hope of making greater headway with the most important problems.

On the more fundamental side, attention has been given to studying the non-rubber substances naturally occurring in latex, which appear to play such a large part in determining the properties of both latex and dry rubber. This is inevitably a long term investigation and no immediate practical developments are to be expected. Considerable progress has been made in isolating and identifying certain constituents of latex protein and of latex phospholipin.

Fundamental studies of the rubber hydrocarbon have been in abeyance, owing to the absence on leave of the officer concerned, although some interesting indications on the changes occurring during storage have been obtained in the course of work on the technical classification of rubber.

Investigations in connection with latex have been concerned mainly with quality, particularly in regard to causes of the inferior properties sometimes shown by commercial concentrates. One of the main factors responsible has been traced and means of overcoming the difficulty investigated. The study of new and improved methods for preserving latex has been continued, including both temporary and long term usage.

Technological investigations of dry rubber have followed two main lines of inquiry. The first of these involved a study of rubber masterbatches prepared from latex by compounding with lignin and with carbon black; the second continued work already in hand on the application of technical classification to Malayan rubber production.

Progress with lignin masterbatching has been somewhat slower than was hoped for, but sufficient advance has been made with latex carbon black preparations to warrant trials being carried out in the United Kingdom.

Progress with the technical classification of Malayan rubber production has been rapid and substantial advances have been achieved. An experimental testing station was set up at the R.R.I. during the year, and the produce of over forty estates was classified, representing an output of some 6,000 tons of rubber, of which over 3,000 tons is known to have been shipped bearing technical class marks on the bales. Further surveys of smallholders' sheet,

packing house production and remilled rubbers have also been carried out. Trials indicated that, given a small modification in packing procedure, it should be possible to classify packing house rubber.

Investigations carried out at the Experiment Station factory covered a wide field, ranging from rapid methods for determining dry rubber content of latex to improved methods for packing sheet rubber.

A number of small *ad hoc* investigations were also undertaken by the Division in connection with advisory work.

For convenience in internal use, the account of investigations given below is divided into sections numbered in accordance with the scheme adopted in the Programme of Research, 1949-53. The numbering does not follow in sequence, as under some headings there are no investigations to report.

I
CHEMICAL & PHYSICAL PROPERTIES OF LATEX & RUBBER

I(1) NON-RUBBER CONSTITUENTS OF LATEX AND RUBBER

Separation from latex — In undertaking an investigation of the non-rubber constituents of latex, one of the most important aspects first to be considered is that, under normal conditions of collection, changes (bacterial, enzymatic and chemical) can occur in the latex immediately after withdrawal from the tree and normally proceed during storage and treatment. In order to ensure that the substances finally isolated from latex are substantially the same as those occurring naturally in the tree, special techniques for collection and separation have to be adopted. Further attention has been given to this problem during the past year and means have been developed for separating latex serum from rubber and of rapidly drying it, so that changes liable to occur in the non-rubber constituents are reduced to a minimum.

For purposes of collection latex is received in vessels maintained at a low temperature. Separation of serum from rubber can then be obtained by keeping latex in the frozen state for 10 to 15 days, by which time the rubber particles have coagulated, and serum can be pressed out from the coagulum. An alternative method of separation has been used in which the cold latex is treated

with a creaming agent and spun in a bucket type centrifuge, when serum can be obtained as a reasonably clear underlayer in a comparatively short time.

In order to free the non-rubber substances from water, the freeze drying technique has been used, in which water is allowed to sublime from the frozen serum under low pressures. A number of modifications of the technique normally used for biological preparations have been necessary in order to handle the comparatively large quantities of serum required; the unit at present in use is capable of drying one and half litres of serum in two days.

Freeze dried preparations of serum have been satisfactorily prepared and have been sealed in glass containers under vacuum before despatch to the United Kingdom, where examination is being undertaken by the British Rubber Producers' Research Association. Samples of other latex fractions, such as sterile latex and the yellow fraction obtained by centrifuging fresh latex, have also been prepared for examination.

As well as developing preparational methods, attention has been given to examining certain particular constituents of latex non-rubber material, *viz,* proteins, phospholipins and lutoids.

Latex proteins — Protein has been separated from latex serum by precipitation with ammonium sulphate; separation into different types was achieved by a differential solubility method, which indicated the presence of albumins, globulins, proteoses, peptones and glutelins. Phosphorus was present in all the fractions isolated. After separation, the protein fractions require to be purified by dialysis, but established methods proved to be slow and led to complications due to oxidation and putrefaction. A modified method was therefore developed in which dialysis is carried out as soon as possible after precipitating the protein, using distilled water at a temperature below 10°C. and maintaining the solutions under nitrogen. Three days continuous operation of the apparatus is required for complete removal of sulphate from the protein. Samples of the dialysed protein have been freezed dried and forwarded to the United Kingdom, where methods of analysis and identification are being studied. It is hoped to examine the materials in Malaya at a later date, when satisfactory techniques have been established.

Phospholipins — Investigations of latex phospholipin have been directed to three main inquiries, (*i*) methods for extraction and purification, (*ii*) changes occurring in the nature of the phospholipin after withdrawal of latex from the tree and (*iii*) the chemical composition of the phospholipin.

In order to separate phospholipin material, RHODES and BISHOP (*J. Rubb. Res. Inst. Malaya* 2 (1930) 125) coagulated latex with alcohol and obtained a fraction rich in phosphorus by acetone precipitation of the aqueous-alcoholic serum. Taking this method as a starting point, a number of modifications have been tried out, the method finally adopted being as follows. Latex is coagulated by running into alcohol under controlled temperature conditions. The alcoholic serum is expressed from the coagulum and evaporated with restricted access of air. Fatty materials are extracted with petroleum ether and water soluble impurities removed by dialysis of an aqueous phospholipin suspension against distilled water. Purification by acetone precipitation has been shown to be unsuitable as part of the phospholipin is soluble in acetone.

If latex is collected from the tree directly into a vessel surrounded by freezing mixture, the phospholipin extracted is markedly more soluble in acetone than that obtained from latex which has been allowed to stand for a few hours at room temperature. Coagulation by hot alcohol of latex collected cold gave a product similar to that obtained from latex stored and coagulated at room temperature. It appears, therefore, that changes in the crude phospholipin proceed in freshly tapped latex on standing at normal temperatures. The change does not appear to be due to hydrolysis leading to the liberation of acid soluble phosphorus, as examination of latex at intervals after tapping showed no appreciable decrease in the petroleum ether soluble phosphorus or increase in the phosphorus content of the serum.

Exploratory experiments to determine the bases present in latex phospholipin have been carried out on hydrolysates, which were analysed by means of paper chromatograms. The presence of choline, serine and ethanolamine has been indicated, together with a number of unidentified ninhydrin-reacting substances. Choline has been estimated as accounting for some 20 per cent of the total phospholipin nitrogen.

Lutoids in latex — The presence in fresh latex of a disperse phase other than rubber was first established by HOMANS and VAN GILS (*Proc. 2nd Rubb. Tech. Conf.* London (1948) 292), who refer to the material as the lutoid fraction. Preliminary investigations carried out in the laboratories of the Chemical Division suggested that this material may play a considerable part in influencing the stability of latex and in the mechanism of spontaneous coagulation. Attempts have now been made to estimate the lutoid content of fresh latex. The method used involves the assumption that the

non-rubber substances may be regarded as comprising three fractions, (*i*) substances associated with the rubber particles, (*ii*) those associated with the aqueous phase, and (*iii*) the lutoids. By estimating the first two, the lutoids are obtained by difference from the total non-rubber substances present, which in turn are estimated as the difference between total solids and rubber hydrocarbon. As it has not been established definitely whether lutoids are associated with water, two possibilities have been considered: (*i*) that the free water present can be estimated by the concentration therein of a non-adsorbed ion (potassium in this case), the remaining water being associated with lutoids and containing no, or a much reduced, ion content, (*ii*) that the water associated with the lutoids can be ignored and that water content may be used to estimate the content of serum solids associated with water as opposed to those associated with rubber globules. It is interesting to note that there was little difference in the values obtained by the two methods; this may be due to the somewhat large inaccuracies in the experimental data.

The results indicated that of the total non-rubber substances in the seedling latex used, 10 to 15% were associated with the rubber particles, and 15% with the lutoids. The wet lutoids appeared to comprise 2 to 5% of the field latex, by weight.

Acid and base content of dry rubber — Work on the non-rubber substances present in dry rubber has been confined to a study of methods for estimating basic and acidic material. No established method for determining base content was available and the solvent extraction method for acids specified by the British Standards Institution was found to give a measure of only half the titratable acidic material present in the rubber. The methods developed in the R.R.I. laboratories involve solution of the rubber in a benzene : ethanol mixture (80 : 20 by volume) and titration with standard perchloric acid solution for base content and with standard sodium ethoxide solution for acid content. The titration can be followed electrometrically using a glass electrode and completing the system by a calomel or silver/silver chloride halfcell. The endpoint for base titrations is usually well defined provided corrections for solution volume are made. A reasonable estimate of base content appears to be given by a colorimetric titration using the development of a pink colour in methyl red as the endpoint. The endpoint for acid titrations using a glass electrode is generally not so definite although a value can usually be obtained by applying the second difference method to the corrected titration curve. Experiments carried out with known amounts of organic acids

showed that the use of a colour indicator is reasonably satisfactory for obtaining an estimate of acid content, the development of the pink colour in phenolphthalein generally being employed. In estimating both base and acid content by a colorimetric method corrections for solution volume and for solvent titre must be made by running a blank titration.

I(4) CHANGES OCCURRING IN AMMONIATED LATEX

A preliminary survey of the behaviour of latex following ammoniation has been commenced, with a view to determining in broad outline the major chemical changes occurring, and if possible to correlate them with the marked changes in physical properties which proceed in freshly prepared latex concentrates.

Experiments carried out so far indicate that a considerable increase in the amount of ether soluble acids occurs during the first week or two of storage, the acids being estimated by extraction from dried films of the latex; this confirms the earlier observation by RHODES (*J. Rubb. Res. Inst. Malaya* 9 (1939) 126) that a marked increase in total acid content occurs during the first few weeks after ammoniation. The present survey has also indicated a release of phosphorus into the latex serum and a decrease in serum magnesium content during the first week of storage.

It has been observed that the marked increase in mechanical stability which proceeds in ammoniated latex concentrate during the weeks following preparation is affected by access of oxygen. Storage of latices under nitrogen or addition of sodium bisulphite tended to slow down the changes occurring, whereas availability of oxygen in the form of hydrogen peroxide had the effect of quickening them. The changes appeared to proceed most rapidly at about 40°C.

I(8) INJECTION OF HEVEA BRASILIENSIS

Experiments to study the effect of injecting *Hevea brasiliensis* with copper and other possible yield stimulants have been planned in cooperation with the Botanical Division; operations were commenced in December. As well as determining the effect upon latex yield, the influence of the injected substances upon properties of the latex and of the dry rubber are being examined.

II(2) QUALITY OF LATEX CONCENTRATE

During the past year a number of complaints have been registered in Malaya regarding the quality of latex concentrate as received in consuming countries. Deterioration of latex during shipment and storage is usually due to the formation of acids, which produce a marked effect upon those properties which concern the manufacturers. In order to check the quality of latex supplies, a simple method, the KOH number test, was developed and has been in use for many years; it is designed to estimate the total acid present in ammonia-preserved latex concentrates as ammonium salts or soaps. Although it is a useful guide, this test gives no information concerning the types of acid present or to their origin.

During the past two or three years. a method of estimating volatile acids in latex has been developed and used in the R.R.I. laboratories; this test gives a measure of lower molecular weight carboxylic acids, the presence of which is largely due to putrefactive processes occurring in the latex.

Recent observations have shown that a high KOH number in commercial concentrates is almost invariably due to the presence of volatile acids; thus for a KOH number of 0.7 to 0.8, 30 per cent is usually accounted for in this way. The presence of volatile acids in latex concentrates results from lack of care in collection, particularly from the use of insufficient ammonia for preservation before processing, and from late ammoniation which allow bacterial infection to occur; there appears to be no reason why a marked improvement in latex quality could not be achieved in many instances by attention to these factors.

Experimental work has demonstrated that the development of volatile acids in lightly ammoniated (0.2 per cent) latices can be inhibited by small quantities of certain bactericides, including formaldehyde. The addition of certain metals known to be enzyme poisons, has been observed to inhibit the formation of volatile acids in latex containing 0.5 per cent ammonia; of a number of metals investigated, zinc added as zinc oxide was the most effective. Although preventing the formation of volatile acids, these reagents did not prevent an increase in the amount of non-volatile acids present, which appeared to form at the usual rate during storage. Urethane, another type of enzyme poisoner, was not effective in hindering deterioration of latex.

Lack of mechanical stability in certain latices, as for instance in that from clone Glenshiel 1, is sometimes a source of trouble in preparing concentrates. Laboratory experiments have established that the addition of small quantities of alkali phosphate is effective in improving this condition. Interesting trials have now been carried out at two estates where the mechanical stability of the concentrates produced was low. A marked improvement in stability was obtained by the addition to field latex of 0.03 per cent lauric acid and 0.03 per cent ammonium dihydrogen phosphate. It is of interest to note that the addition of too much phosphate (in one series of experiments, more than 0.1 per cent) has the effect of reducing the mechanical stability of latex concentrates.

II(3) LATEX TESTING METHODS

Collaboration with the British Standards Institution Latex Sub-Committee, RUC/10/7, has been maintained in developing latex testing methods, experimental work having been carried out in connection with the mechanical stability test and with the determination of copper in latex.

In studying the mechanical stability test, it was found that the use of plastic containers as suggested by the International Standards Organisation at the Akron Meeting, October 1950 (Resolution 161), is open to the objection that a considerable rise in temperature can be obtained in the course of the test, when working under tropical laboratory conditions.

II(4) PRESERVATION OF LATEX

Further work on the use of formaldehyde as a temporary preservative for latex has confirmed earlier observations, that in the presence of mild alkalies, such as sodium carbonate, satisfactory preservation can be obtained. Using this system a trial was carried out in cooperation with a commercial organisation in which latex was successfully transported over a distance of more than 100 miles and then processed into pale crepe; the crepe was somewhat soft, but had a reasonably good colour. It is hoped to carry out further large scale trials along these lines with a view to improving the quality of the crepe produced.

In the course of earlier work directed towards preservation of latex under neutral conditions, it was observed that preservatives of the polyglycol ether type were often satisfactory, although they had to be used in large amounts. These materials are also heat sensitive in respect of solubility and attempts have now been

made to produce a heat sensitive latex, which would coagulate on formers at a given temperature. This has been found possible, but only a few of the reagents tested afforded adequate preservation of latex and these required to be present at high concentration. None will maintain the latex at a pH value in the region of 7.0 without the presence of a bactericide.

Investigations to develop improved methods for preservation of latex concentrates have continued, and two promising systems are under trial in the United Kingdom at present. Both methods employ ammonia at considerably lower concentrations than normal, and depend upon the addition of further reagents for effective preservation.

II(5) DISCOLOURATION OF RUBBER FROM SANTOBRITE LATEX

One of the difficulties experienced by manufacturers in employing latex concentrates preserved with sodium pentachlorphenate, is the dark colour shown by dry rubber films prepared with the latex. It has frequently been observed in these laboratories that unvulcanised rubber films prepared by drying down latices to which sodium pentachlorphenate has been added show marked discolouration compared with the untreated material: more recent observations have shown that similar discolouration is brought about in latex films by a number of reagents, particularly by detergents. The discolouration is intensified by the addition of tyrosine and, in general behaviour, the phenomenon is very similar to that produced when tyrosine is oxidised by tyrosinase. The discolouration can be inhibited by the presence of 0.025 per cent of thio-urea or of 0.05 per cent sodium bisulphite, based on the latex.

Examination of a number of latices has demonstrated that those from certain clones do not show discolouration of the dried films when preserved with sodium pentachlorphenate.

Trials are at present being made in collaboration with the L.A.C. to determine whether the discolouration complained of by latex consumers is that described above in films from freshly prepared latices.

III
CHEMISTRY & TECHNOLOGY OF DRY RUBBER

During the year, work on the technology of rubber has been concerned with two main problems, (*a*) methods of preparing and

testing rubber masterbatches prepared from latex by mixing in lignin or carbon black prior to coagulation and drying, and (*b*) development work associated with the technical classification of Malayan rubber production.

III(6) MASTERBATCHES PREPARED FROM LATEX WITH LIGNIN OR CARBON BLACK

Work on rubber lignin masterbatches was confined to a few preliminary experiments in which an attempt was made to correlate the reinforcing behaviour of lignin with physical properties such as melting point and specific gravity, and with the degree of oxidation of the lignin. No positive conclusions could be drawn from these investigations. It was observed, however, that compounds containing Indulin A, a lignin of Canadian origin, possessed high resistance to tear.

The major part of the investigation was concerned with rubber carbon black masterbatches, with a view to examining the possibility of large scale production. The advantage of producing raw rubber carbon black stocks in this form is that the operation of milling in the black in the tyre factory is avoided, thus saving time and power. Synthetic rubber carbon black compounds are already marketed in this form. There is also the possibility that owing to the reduced time of milling necessary, less breakdown of the natural rubber hydrocarbon would occur and a superior product would be obtained.

If an aqueous suspension of carbon black (MPC) stabilised with a lignin sulphonic acid salt or similar reagent is added to fresh latex, a mixture is obtained which can be coagulated by stirring, with or without the addition of acid, to give a loosely cohering, crumb coagulum. Almost all the black is retained in the coagulum, which can be tray dried as a crumb or machined to give a rough, loosely cohering sheet, and hung to dry in the usual way. Sheeting of the coagulum is assisted by adding to the latex black mixture a softener such as pine tar, which is normally used in preparing tyre tread compounds. The dried material has a remarkably clean handle.

Tyre tread compounds were prepared from this material by dry milling with the required vulcanising ingredients, but, after vulcanising, showed properties somewhat inferior to those normally obtained with dry mixed stocks. Factors affecting the properties of vulcanisates prepared from rubber carbon black masterbatches were then investigated.

One of the most important factors was the degree of dispersion of the carbon black in the rubber, as judged by viewing microscope sections. For instance, very high modulus vulcanisates resulted from masterbatches prepared by mixing latex with finely dispersed black suspensions obtained by ball milling; it was not found possible to produce such high modulus stocks by dry mixing. It was observed, however, that with increasing fineness of dispersion of the black, the resilience of the vulcanisates decreased.

Other factors such as coagulation at different dry rubber contents of the latex, or changing the concentration of the black suspension, had no appreciable effect upon the properties of vulcanisates, although ease of preparation of the masterbatches was considerably influenced. There was some evidence that differences in properties after vulcanising were obtained by using seedling and clonal latices, but further work is needed before these effects can be established.

An interesting series of vulcanisates has been made from masterbatches containing different proportions of rubber to black, the additional amount of rubber or black necessary to give a stock of the proportions required for a tread compound being added on the mill during the mixing operation. Considerable variation in the specific gravity of the compounds was observed, although analysis showed the proportion of rubber to black to be the same throughout the series. On examination it was found that a considerable decrease in scorching time occurred as the proportion of black in the masterbatch increased. The results of physical tests on vulcanisates suggested that modification in tension strength, modulus, resilience and hardness may be brought about by using masterbatches of different composition.

Work is at present in hand adapting the method of preparation to larger scale production, when samples of the masterbatch will be forwarded to the United Kingdom for examination by manufacturers.

III(7) TECHNICAL CLASSIFICATION OF NATURAL RUBBER

The major project planned for 1951 in connection with the technical classification of rubber, was to make available from Malayan estates large quantities of classified RSS 1 so that manufacturers could evaluate the method of classification.

Classification of estate rubber — During the year contact was made with 88 estates, 69 of which signified willingness to cooperate; of these, 42 were allocated technical class marks during 1951 after tests had been carried out on the level and variability of production. In all, the samples tested during 1951 represented an output of some 6,000 tons of rubber from estates cooperating with the Rubber Research Institute, of this 3,144½ tons was actually shipped bearing technical class marks on the bales. At the end of the year, samples representing an annual output in excess of 10,000 tons per annum were being received from the 36 estates already classified and actively cooperating.

In order to deal with the relatively large volume of testing involved (between July and December well over 5,000 samples of rubber were examined), a laboratory was set up to function as a self contained testing station. This arrangement also permitted an assessment to be made in respect of staff, equipment and expenditure likely to be involved in the technical classification of estate rubber. As far as can be estimated at the time of writing the cost to the industry is not likely to be in excess of one eighth of a cent per pound of rubber classified, for estate smoked sheet.

Classification of smallholders, packing house and remillers rubbers — As well as classifying estate rubber, attention was also given to the problems of classifying smallholders' production, sheet from packing houses, and crepe from remilling factories. A small scale preliminary survey was carried out on smoked and air dried sheet from 143 smallholdings. The data suggested that in respect of Mooney viscosity smallholders' sheets showed greater heterogeneity than those from estates. For vulcanised properties, highly significant differences between smoke houses were observed, as well as significant variation between sheets.

For packing house rubber, earlier work revealed the high variability between bales produced on a given day, and that modification in packing methods might be required before a satisfactory technique of classification could be developed. Recent experiments carried out along these lines in cooperation with a commercial organisation have demonstrated that a considerable reduction can be obtained in the bale to bale variability. Further work is in progress to establish a packing procedure which is suitable for commercial practice and at the same time lends itself to the application of technical classification.

Two surveys of remilled rubbers have been carried out. Marked variability, both within and between bales, suggests that

further large scale surveys may be necessary before technical classification can be applied satisfactorily to these grades.

Variability of estate rubber — A considerable amount of small scale experimental work was undertaken at the Institute's Experiment Station to determine some of the sources of variability in the production of smoked sheet. It was shown that small scale bulking of latex greatly reduced variability; small but significant differences in properties were found still to exist, both between sheets from different coagulating tanks and between sheets within a coagulating tank. These differences are not likely to be of technical importance.

Coagulation of latex at different dry rubber contents within the range of one pound to one and three quarter pounds per gallon had little effect upon either the Mooney viscosity of the raw rubber or the properties of mercaptobenzthiazole vulcanisates. Comparison of sulphuric and formic acids for use in coagulation showed no observable difference as judged by these tests. The use of ammonia as an anticoagulant in the field gave a small but significant increase in Mooney viscosity of the raw rubber; the addition of ammonia also increased the modulus of mercaptobenzthiazole vulcanisates, particularly when formic acid was used as a coagulant.

Small scale experiments indicated that the addition to latex of small quantities of certain quaternary ammonium salts, such as 0.01 per cent dodecyl pyridinium bromide, was an effective method of increasing the modulus of smoked sheet, when compounded according to the A.C.S. No. 1 formulation. The increase in modulus was only slightly reduced by the presence of formaldehyde, added to the latex as an anticoagulant.

Laboratory investigations of methods of testing have established satisfactory schedules for blending of samples and for mixing of compounds on laboratory mills to give a reasonably standard Mooney viscosity of the compounded stock. Experiments to check tension testing equipment with other laboratories in Malaya and in the United Kingdom demonstrated good agreement for strain tests carried out at low elongation, but poor agreement for high elongation modulus testing.

Changes in Mooney viscosity on storage — An interesting problem, to which considerable attention has been given, arose in connection with the Mooney viscosity of raw rubber. It was observed that marked changes in the Mooney value proceeded during storage, thus greatly reducing the value to consumers of rubber

classified in Malaya according to this property. The factors underlying the changes on storage were investigated. Increases in Mooney viscosity of the order of 30 to 40 units were found to proceed in freshly prepared raw rubber when it is stored at low relative humidity. The rate, as well as the extent of the change, was greatest in the region below 30 per cent R.H. The rate of change in dry air increased with temperature, although the effect was masked by oxidative breakdown on prolonged storage at elevated temperatures. Although storage in dry air was necessary for marked increases in Mooney viscosity, the changes proceeded long after the rubber was dry and cannot thus be considered as due to the mere physical presence or absence of moisture. Removal from the rubber of acetone soluble and of nitrogenous material had no appreciable effect upon hardening under dry storage. The changes proceeded in a similar manner when rubber was dry stored in absence of oxygen. Masticated rubber behaved like raw rubber. Smoked sheet rubber hardened by this means showed a more rapid mill breakdown than normal sheet, but when processed under standardised conditions gave a compounded stock with a higher Mooney value. The physical properties of vulcanisates which were prepared from compounds milled to the same Mooney viscosity demonstrated a slight superiority for hardened rubber as compared with normal smoked sheet.

It is of interest to note that the hardening produced by dry storage was only partially reversed by subsequent storage at high humidity. Humidity variation in smoke houses and drying sheds may thus account for part of the Mooney viscosity variability of natural rubber production. It was found that by further 'drying' of dry smoked sheet in a hot air chamber, a permanent increase in Mooney viscosity was obtained.

IV
PREPARATION PRACTICE

IV(1) FACTORY PROCEDURE

Approximate methods of determining dry rubber content — A rapid means for determining the dry rubber content of latex is an essential part of factory procedure. The most common methods employ hydrometers, but results obtained with these instruments are not very reproducible. Recent experiments have shown that with the Simplexometer, for instance, the standard deviation of a

determination was about 0.15 lb per gallon. The variance of Simplexometer estimates was significantly greater than the variance of estimates obtained by weighing the sheet prepared from a known volume of latex; laboratory determinations using the British Standards Institution method also gave a lower variability. Further work demonstrated that a large part of the variability in Simplexometer measurements was due to inaccuracies in measuring out both latex and water, when diluting the latex for test.

It has been suggested that the dry rubber content of field latex could readily be estimated by coagulating a known quantity of latex, and weighing the machined coagulum after a fixed time, a standard correction being applied for water content. Experiments have shown that the rate of water removal from machined coagulum, when hung, is dependent upon the dry rubber content of the original latex and varies from day to day. It appears, therefore, that this method would not be particularly reliable.

A more accurate method (the Chee method) for the rapid estimation of dry rubber content has been studied, in which a known volume of latex is delivered by a dipper, coagulated, dried, and weighed on a simple balance. Statistical examination of experimental data comparing different types of dipper gave preference to a long narrow type which, however, has the disadvantage that it is not so readily cleaned.

Behaviour of latex during coagulation — It is of considerable importance in factory practice to know the behaviour likely to be experienced when coagulating a given bulk of latex. Whereas the behaviour of latex from any particular task on an estate is usually wellknown, the effect upon coagulation of adding anti-coagulants and temporary preservatives has not been established with any certainty.

From earlier experiments (1948) it is known that after mixing with acid, latex viscosity increases linearly with time for a period, after which the plot becomes curved, showing greater rates of increase of viscosity with time; this is soon followed by coagulation. Simple practical tests have now been devised which measure the time to produce a given thickening in the latex and the time required to give a coherent coagulum. At this stage the coagulum, although coherent, is very weak mechanically, but becomes stronger on standing, during which time marked syneresis occurs. No simple means for evaluating behaviour during this process has yet been developed.

Using these practical methods for assessing behaviour during coagulation, the following observations were made on latex collected as normal crop at the Institute's Experiment Station:

(*i*) The coagulation time of fresh latex decreased with storage, until spontaneous coagulation occurred.

(*ii*) The addition of 0.05 per cent formaldehyde to latex caused an immediate decrease in coagulation time, which then remained more or less constant until the latex finally coagulated spontaneously, usually some 24 hours later than the untreated latex.

(*iii*) The addition of 0.05 per cent ammonia to latex brought about an immediate and marked increase in coagulation time. For instance the period increased from 10 to 100 minutes. The coagulation time then decreased steadily and the latex finally coagulated 3 to 6 hours after the untreated material.

Coagulants for latex — In the course of the year a number of observations have been recorded upon the use of different coagulants in the preparation of smoked sheet.

Continuing work on sulphuric acid coagulation, no appreciable effect upon hardness of raw rubber or upon modulus of vulcanisates was found when sulphuric acid was used on an estate to replace formic acid in the preparation of smoked sheet.

During 1951 sulphamic acid was offered by commercial suppliers as an alternative to formic or acetic acids. Trials in the laboratory and on a larger scale at the Experiment Station showed the material to be a satisfactory coagulant, although double the quantity was required in comparison with formic acid. Properties of the vulcanised rubber prepared with the sheet appeared to be normal. As the price of sulphamic acid was similar to that of formic acid, the experiments were not continued.

The use of alum as a latex coagulant has not been recommended in Malaya on the grounds that it gives rise to rubbers showing high moisture content, poor ageing characteristics and decreased rate of cure. The results of technical tests carried out on smoked sheets prepared from alum coagulated latex have now been received from the Research Association of British Rubber Manufacturers. No evidence was found that either ammonium or potash alum coagulation affected the properties of tyre tread vulcanisates, which were not appreciably different from those given by formic acid coagulated sheet.

Drying of smoked sheets — Preliminary experiments have been carried out to trace the source of variability in the drying

time of smoked sheets. In one trial, 37 per cent of the sheets were completely dry after three days in the smoke house, but the remainder showed white wet patches and took considerably longer to dry. The wet patches appeared to be more frequent along the edges corresponding to the upper edges of the original coagula, and careful observation employing photographic records indicated that, after drying, the areas associated with the wet patches were appreciably thicker than the surrounding sheet. There was no evidence that the wet patches were due to drainage of water to the areas in question. The data thus suggest that if more even sheeting could be achieved a saving in drying time should result.

It is hoped to carry out a more exhaustive investigation of the factors affecting the drying of coagulum, and detailed designs for an experimental drying tunnel have already been completed.

R.R.I. 'bleaching' process for preparing pale crepe — Earlier observations showed that mercaptans are effective in destroying the colour of the yellow pigment naturally present in latex. Trials established that satisfactory pale and sole crepe could be prepared from whole latex using these 'bleaching' reagents, thus avoiding fractional coagulation. In order to make the process available for use on estates, the Division undertook the preparation of an emulsion containing xylyl mercaptan, which was marketed through one of the well known estate suppliers. During the year the following quantities of the emulsion were prepared:

First Quarter	...	...	...	ca 900 gallons
Second Quarter	...	...	...	1,400 gallons
Third Quarter	...	...	...	1,856 gallons
Fourth Quarter	...	...	...	2,144 gallons

The total quantity of emulsion was sufficient to treat well over 6,000,000 lb of crepe.

Experimental work has been carried out in cooperation with the manufacturers of the 'bleaching' reagent with a view to producing the material in a form which can be emulsified directly on estates. It is hoped that this new material will be commercially available towards the middle of 1952.

Although very satisfactory crepe can be prepared using the 'bleaching process', it is necessary to ensure that only the minimum quantity of the reagent required to give a good white colour is employed, as soft and dull coloured products may result if excess emulsion is used.

Fungicides for sheet rubber — Preliminary trials with fungicides for air dried sheet led to the interesting observation that at the 0.1 per cent level a solution of p-nitrophenol (PNP), was more

effective than a solution of sodium pentachlorphenate (Santobrite), whereas at the one per cent level, the reverse was true. Solutions of a proprietary quaternary ammonium salt were quite ineffective at one per cent concentration. The trials were not carried out under conditions of controlled innoculation, and the results must therefore be treated with reserve.

IV(2) PACKING, BALING AND MARKETING

It is proposed to carry out a series of packing trials by shipping bales prepared and packed at the Experiment Station factory to a depot in the United Kingdom where examination can be undertaken by members of the staff of the London Advisory Committee. In the course of the experiments it is hoped to cover many different aspects of packing, but early attention will be given to problems connected with bale coating compositions and stencil inks.

For preliminary evaluation in the laboratory a readily standardisable test has been developed, which permits a rough estimate to be made of the resistance of bale paints and stencil inks to stretching and attrition. Using this method, the following coating compositions have been compared: (*a*) the Socfin standard aqueous paint (Rubber Research Institute of Malaya, *Planting Manual No. 10,* August 1951), (*b*) a modification of the Socfin paint, employing ammonium alginate (Superloid) in place of starch as a binder, and (*c*) R.M.A. type bale paints, in which lower proportions of talc to rubber were employed so as to obtain a less powdery surface.

The standard Socfin aqueous paint showed good resistance to rubbing and stretching, but the modification containing alginate in place of starch was inferior to the other mixtures examined. The most suitable type of R.M.A. paint was one having a ratio of talc to rubber one quarter of that recommended in the standard formula, as given in the *Temporary Packing Specifications for Crude Rubber,* 1951.

It should perhaps be emphasised that these results were obtained using laboratory tests, the value of which has yet to be established by practical shipping trials.

IV(3) NEW PROCESSES

Line ahead creping battery -- Earlier experiments demonstrated the feasibility of producing crepe on a line ahead principle similar to that in use for continuous sheet manufacture. Arrangements for constructing a prototype machine along these lines were made during 1950. Part of the machine (Part II) was completed in the

latter half of 1951 and was installed in the Chemical Division Factory at Sungei Buloh. Owing to the large cost involved, it was decided not to proceed with the construction of the remainder of the prototype machine (Part I), but to purchase suitable secondhand plant, and to overhaul and adapt it for the purpose. At the end of the year the required secondhand machines had been obtained and arrangements made for overhaul and adaptation. It is doubtful whether Part I of the battery will be ready for installation before mid 1952 owing to the difficult supply position for certain essential items.

Continuous process for preparing dry rubber — Work on the L.A.C. scheme for preparing dry rubber by a continuous process has continued at intervals throughout the year, although it has been possible to devote only a little time to this project. The object of the experiments carried out was to determine some of the factors responsible for the very soft coagulum produced with fresh as compared with ammoniated latex. A simple test, which measures the distension of a thin film of coagulum produced under a standard load, established that latices from which non-rubbers have been largely removed gave coagulum films showing considerably greater resistance to stretching. Replacing protein by the addition of casein to the latex gave rise to coagulum films approaching the original whole latex ones in ease of stretching. The experiments thus indicate that low resistance to deformation in latex coagulum is conferred by the presence of naturally occurring protein. Further work is in hand with a view to overcoming this difficulty.

IV(4) LARGE SCALE PREPARATION OF SPECIAL RUBBERS

Rubber powder — Following the decision of the Board early in March to manufacture rubber powder at the Experiment Station factory according to the Mealorub process, makeshift plant was erected and production commenced during June. Since that time output has been maintained at a rate of 8½ tons per month, some 55 tons having been produced by the end of the year.

In the early stages, complaints were received from the consignees due to massing of the powder during shipment; this was overcome quite successfully later in the year, by the addition of 2 to 3 per cent talc to the powder before packing.

The technique of preparation now in use closely follows the method published by the Indonesisch Instituut voor Rubberonderzoek in *Bericht* No.102, 1949, although minor adaptations to local

conditions have been made. For purposes of heating, injection of steam directly into the latex has been found preferable to the use of a steam jacketed reactor. De-watering of the coagulum can be achieved satisfactorily by squeezing the coagulum slurry in folded canvas under a bale press, in place of the cylinder and plunger recommended in the Indonesian publication. Drying of the crumb is largely carried out on trays in a Socfin type drier, instead of the rotary type drier as recommended; tray drying, however, does not prevent the powder from massing as does a rotary drier and a further passage through the disintegrator is necessary to obtain a freely flowing product. The powder is finally packed in plywood cases.

During 1951 the nett cost of production and packing at the Experiment Station amounted to about 22 Straits cents per pound above the cost of the latex used.

Laboratory reports on the product have been favourable, but accounts of its behaviour when incorporated with bitumen in actual road practice have not yet been received.

ADVISORY WORK

THE VOLUME OF GENERAL ADVISORY WORK remained much the same as during the previous year, save that fewer requests to visit estates were received. Office records show the following:

Interviews, Headquarters & E.S. factory ...	306
Visits to Estates	130
Letters and Reports	2,466
Samples examined (excluding those examined in connection with Technical Classification) ...	1,648

Pamphlets issued:

C/M.89(51) — Proposed Technical Organisation of Natural Rubber Producers, Malaya. Progress Report No.4.

C/AL.14(51) — The Preparation of Rubber Powder (Mealorub) on Estates.

OTHER ACTIVITIES

A LATEX SYMPOSIUM was held at the R.R.I. in February; members of the Division assisted with the organisation and contributed 15 papers.

The Division has continued to serve as liaison between the Committee of Malayan Latex Technologists and the British Standards Institution Sub-Committee RUC/10/7, dealing with latex testing methods.

Construction of the new laboratories at Sungei Buloh was approaching completion at the end of the year; equipping with laboratory furniture and the required services will probably entail another six months before the building is ready for occupation.

The new factory at Sungei Buloh was nearly completed at the end of 1950, and was already processing the estate crop. During 1951 most of the equipment has been tried out in large scale production and found to be satisfactory; extended trials for the prepartion of latex concentrates were not undertaken owing to the difficult market position. Experimental work on crepe rubber was severely handicapped because the line ahead creping battery was still incomplete at the end of the year; a new scrap creping battery, ordered in September 1950, was not installed until November 1951, and broke down in December.

Work connected with the erection and running of the plant for preparing rubber powder occupied a substantial proportion of the time of the Chemical Engineer and of the factory staff.

PUBLICATIONS

DURING THE YEAR the following publications were issued:

'Studies in Hevea Rubber' Parts I to VI by G.F. BLOOMFIELD, *J. Rubb. Res. Inst. Malaya* 13 (1951) (Communications 271, 272 & 273).

Contributions to the Latex Symposium held at the R.R.I. in February, abstracts of which were published in the Institute's Journal, Vol.13, Communication 276 of December 1951 were as follows:

Characteristics of Rubber in Latex of Untapped Trees and in Branches of Trees in Regular Tapping — G.F. BLOOMFIELD

The Rubber Hydrocarbon in Hevea Latex — G.F. BLOOMFIELD

A Note on the Phosphatase in Latex	CHEAH SEIN LIAT
The Lutoid Fraction and the Stability of Hevea Latex	A.S. COOK and A.I. MCMULLEN
The Pre-coagulation of Hevea Latex in Wet Weather	A.S. COOK and A.I. MCMULLEN
The Temporary Preservation of Hevea Latex	A.S. COOK
The Determination of the Inorganic Constituents of Hevea Latex	G.W. DRAKE
The Amino Acid Constituents of the Protein of Hevea Latex	G.W. DRAKE
The Extraction of Latex under Sterile Conditions and Some Properties of Sterile Latex	A.I. MCMULLEN
Some Aspects of Theories of Spontaneous Coagulation	A.I. MCMULLEN
The Preservation of Latex at Neutral pH	A.I. MCMULLEN
The Structure and Strength of Fresh Coagula	A.I. MCMULLEN
Latex Stability and Composition	M.W. PHILPOTT *et alia*
The Determination of Volatile Acids in Latex	M.W. PHILPOTT and K.C. SEKAR
A Note on the Fractional Separation of Latex Proteins	B.C. SEKHAR and A.I. MCMULLEN

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Kuala Lumpur
12 June 1952